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Reducing Film Thickness in Lead Zirconate Titanate Thin Film Capacitors

by Vikram Rao and Ronald G. Polcawich

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14. ABSTRACT
The goal of this project is to characterize the dielectric and ferroelectric performance of lead zirconate titanate (PZT) thin film capacitors as a function of film thickness and sol-gel solution composition. For the thickness experiments, the underlying silicon dioxide, platinum electrode, and the spin-deposited PZT thicknesses were varied. For the solution tests, the molarity and the zirconium/titanium ratio was also varied. In addition, PZT spin rate was varied to determine the spin rate's effect on PZT thickness and dielectric and ferroelectric properties. Both capacitance and hysteresis data were taken for all samples. This project will aid the Defense Advanced Research Projects Agency (DARPA) nanoelectromechanical switch (NEMS) program by investigating avenues of reducing film thickness while maintaining acceptable levels of performance.

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PZT, Thin Film, Ferroelectric, Capacitors

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1. Introduction

1.1 Motivation

The purpose of this project was to investigate the effect of reducing the thickness of the dielectric, platinum electrode layers, and lead zirconate titanate (PZT) thin film in PZT ferroelectric capacitors. To test the nature of this relationship, capacitance and ferroelectric data were taken from three sample wafers with varying layer thicknesses on each wafer. Another set of testing was conducted to investigate the performance of different PZT solution molarities and spin rate on PZT film thickness and the ferroelectric and dielectric characteristics of the PZT capacitors. The results from this project will provide critical information to the Defense Advanced Research Projects Agency (DARPA) funded nanoelectromechanical system (NEMS) switch program. The goal of the NEMS program is to create switches small enough to be combined with complementary metal-oxide semiconductor (CMOS) transistors to improve the leakage power of the transistor.

1.2 Ferroelectric Property of PZT

PZT is a ceramic with chemical formula $Pb[Zr_xTi_{1-x}]O_3$, which is frequently employed as a capacitor dielectric because of its ferroelectric properties. In addition to a high dielectric constant, a ferroelectric material possesses a spontaneous polarization that can be switched by a strong external electric field. A related phenomenon is the tendency for ferroelectrics to exhibit a polarization hysteresis as a function of applied electric field. A typical hysteresis loop plots a ferroelectric sample's net polarization against the applied electric field. The critical features, shown in Figure 1, are the remanent polarization P_r^+ and P_r^-, which describes the remaining net polarizations when the field is brought back to a zero electric field, for both positively and negatively poled samples. For this research, the capacitance and ferroelectric hysteresis loop characteristics will be measured as a function of PZT film thickness and as a function of underlying metal and dielectric thin film thicknesses.

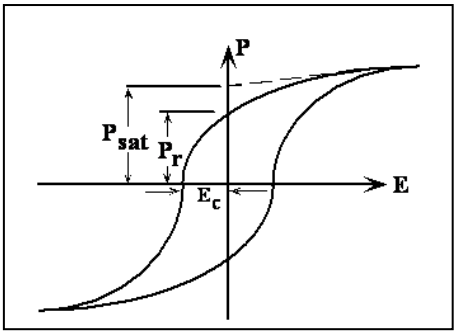

Figure 1. Typical P-E ferroelectric hysteresis loop.[1]

2. Experiment and Calculations

2.1 Sample Preparation

For the first test, all wafers were fabricated beginning with 100 mm silicon substrates followed by conformal deposition of silicon dioxide (SiO_2), titanium (Ti), platinum (Pt), and PZT thin films of varying thickness. The layer thicknesses for each of the tested wafer samples can be found in tables 1 and 2.

Table 1. Varying substrate layer thicknesses.

Wafer ID	SiO_2 (Å)	Ti (Å)	Pt (Å)
2151	2251	200	820
2174	2251	50	500
2156	165	50	500

[1] Adapted from Jaffe, B.; Cook, W.R.; Jaffe, H. *Piezoelectric Ceramics*, R.A.N., Ohio, 1971.

Table 2. Varying PZT thicknesses.

Sample	Number of PZT Spins	Thickness (μm)
2151-1A	8	0.3966
2151-1B	7	0.3332
2151-1C	6	0.2873
2151-1D	5	0.2367
2151-1E	4	0.1869
2151-1F	3	0.1359
2151-1G	2	0.0808
2151-1H	1	0.0461
2174-3A	8	0.38471
2174-3B	7	0.33446
2174-3C	6	0.28483
2174-3D	5	0.23894
2174-3E	4	0.18189
2174-3F	3	0.13815
2174-3G	2	0.14456
2174-3H	1	0.04483
2156-5A	8	0.3893
2156-5B	7	0.33912
2156-5C	6	0.28835
2156-5D	5	0.24164
2156-5E	4	0.18686
2156-5F	3	0.15315
2156-5G	2	0.14456
2156-5H	1	0.044762

The SiO_2 thin films were deposited by plasma enhanced chemical vapor deposition followed by a rapid thermal anneal at 700 ºC in 5 standard cubic centimeters per minute (sccm) of flowing nitrogen (N_2) for 60 s. The Ti and Pt films were deposited by direct current (DC) magnetron sputtering at 500 ºC with the Pt thin film deposited immediately following the Ti thin film without exposing the wafer to the ambient conditions. Following the metal deposition, the wafer was cleaved into eight samples approximately 1.5 cm × 1.5 cm in area. Each sample was coated with sol-gel PZT thin films of varying thickness from 1 to 8 spin layers. Each PZT layer was spin-deposited at 3000 revolutions per minute (rpm) for 30 s. After spinning, the samples were placed onto a hot plate at 350 °C for 2 min to remove the volatile organics. The sample was then cooled on small piece of aluminum. Finally, the PZT was crystallized using a rapid thermal anneal (RTA) at 700 ºC for 30 s in flowing compressed dry air. After the wafer was cooled to room temperature, 1050 Å of Pt was sputter deposited onto the sample surface at 300 ºC. Following the Pt deposition, the process to define the PZT thin film capacitors began by coating

the sample with 5214-E photoresist. The photoresist was patterned with an array of 500 μm × 500 μm squares of resist.

After developing the photoresist, the samples underwent a 2 min oxygen plasma descumming process to remove photoresist residues. Next, the resist was cured using a combination of ultraviolet (UV) illumination and temperature (220 ºC). The UV-cured resist helps prevent heavy metal ion implantation that can occur during the argon ion-milling process used to remove undesired regions of Pt on top of the PZT. Following the ion-milling process, the remaining resist was removed with a 25 min oxygen plasma. To open a window to the bottom Pt, another layer of resist was coated onto the sample. Next, a corner of the sample was wiped clean with acetone to remove the photoresist. Subsequently, this corner was exposed to a wet-etch bath consisting of H_2O:HCl:HF (2:1:0.05) to etch the PZT revealing the underlying platinum layer. Following the wet etch of PBT, the resist is removed using Acetone. Next, the samples undergo a rapid thermal anneal at 350 °C in 5 sccm of flowing compressed dry air for 120 s. The anneal serves to remove any sputter induced surface damage and improve the PBT interface.

For the spin rate test, the process was varied slightly: 100 Å of Ti and 850 Å of Pt were sputtered onto the silicon dioxide coated wafer at 300 ºC. The wafers were cleaved into 1.5 cm × 1.5 cm samples to create a total of 15 test specimens. These specimens were then coated with either sol-gel PZT solution 190, 191, or 192 and spun to a PZT thickness of ~ 4000 Å at spin rates of 1, 2, 3, 4, and 5 krpm (kilo rotations per minute). The actual thicknesses are located in table 3. The remainder of the sample preparation process was similar to that of the thickness tests except that the spin rate samples did not undergo descumming or ion milling to define the top Pt metallization. Instead the top Pt was patterned using a photoresist liftoff process using Pt sputter deposited at room temperature.

Table 3. Final PZT thicknesses for spin rate test.

Sol-gel PZT Solution	1000 rpm	2000 rpm	3000 rpm	4000 rpm	5000 rpm
190	4051.5 Å	3871.5 Å	4419.4 Å	3977.5 Å	3786.6 Å
191	Bad Sample	Bad Sample	Bad Sample	Bad Sample	Bad Sample
192	4636.5 Å	3749.2 Å	4596.1 Å	4102.4 Å	3903.4 Å

For the PZT solution test, three different samples with varying sol-gel PZT solutions were prepared using the same process as the thickness test. The solutions varied in their zirconium (Zr) to Ti ratio and overall molarity. Table 4 gives the exact solution composition.

Table 4. Various Sol-gel PZT solutions.

Sol-gel PZT Solution	Zr/Ti Ratio	Molarity (M)	Test Sample Thickness (µm)
190	45/55	.367	0.5246
191	45/55	.12	0.39724
191 (2221)	45/55	.12	0.19022
192	52/48	.587	0.80973

2.2 Tests and Test Equipment

The capacitance measurements were taken with a Hewlett-Packard 4275A LCR meter. The ferroelectric measurements were taken with the Radiant Technologies RT-66i ferroelectric test setup, which works by stepping though a series of voltages in a triangular bipolar waveform. At each step, the current induced in the sample is integrated to obtain a charge, which combined with sample area information, is used to calculate polarization. For these tests, a pair of micromanipulators or probes are used to make contact with the bottom and top platinum layers as shown in figures 2 and 3.

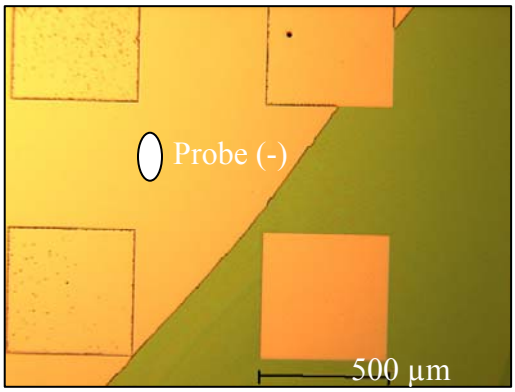

Figure 2. Wet-etched region (bottom Pt electrode).

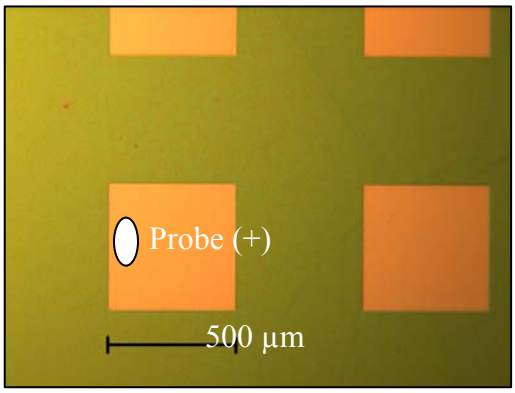

Figure 3. Test capacitor (top Pt electrode).

2.3 Procedure

2.3.1 Dielectric and Ferroelectric Tests

The first test investigated the properties of the capacitors as a function of PZT thickness. Both dielectric and ferroelectric measurements were taken from each wafer for samples of varying numbers of PZT spin depositions (varying thicknesses). Micromanipulator probes were contacted with the exposed bottom Pt and individual top Pt terminal of each capacitor. Using the LCR meter, capacitance measurements and dielectric loss tangents were taken at 10 kHz with a 50 mV_{AC} input signal. A hysteresis loop was then obtained using the ferroelectric test equipment. The setup required input of the capacitor's area, thickness, and desired peak voltage to run the hysteresis test. All capacitors had an area of 0.0025 cm^2. The peak voltage was normalized against film thickness (8 spins: 19V, 7 spins: 16.625V, 6 spins: 14.250V, etc.) to ensure a somewhat constant electric field. Dielectric and ferroelectric tests were repeated for eight test capacitors on each sample to obtain mean and standard deviation values.

2.3.2 Sol-gel PZT Solution Test

The second test investigated the dielectric and ferroelectric properties of samples spun with the different PZT solutions (190, 191, and 192). The same testing procedure was used with the peak voltage of the ferroelectric test once again being normalized against thickness, which was different between the samples. Dielectric and ferroelectric tests were repeated for eight test capacitors on each sample.

2.4 Calculations

The dielectric constant was calculated for each capacitor using equation 1, where C is capacitance, t is film thickness, and A is capacitor area.

$$\varepsilon = \frac{C \cdot t}{\varepsilon_0 \cdot A} \tag{1}$$

3. Results and Discussion

3.1 Thickness Tests

Wafer 2151 yielded usable results from 8 to 4 spins of PZT. At 4 spins, remanent polarizations were 14.74 and -14.43 μC/cm^2, for the two polarization states, and the dielectric constant was 844, within the acceptable range (800-1200), see figure 4. At 3 spins (sample 1F), however, both remanent polarizations (10.30 and –10.92 μC/cm^2) and dielectric constant (457) dropped sharply.

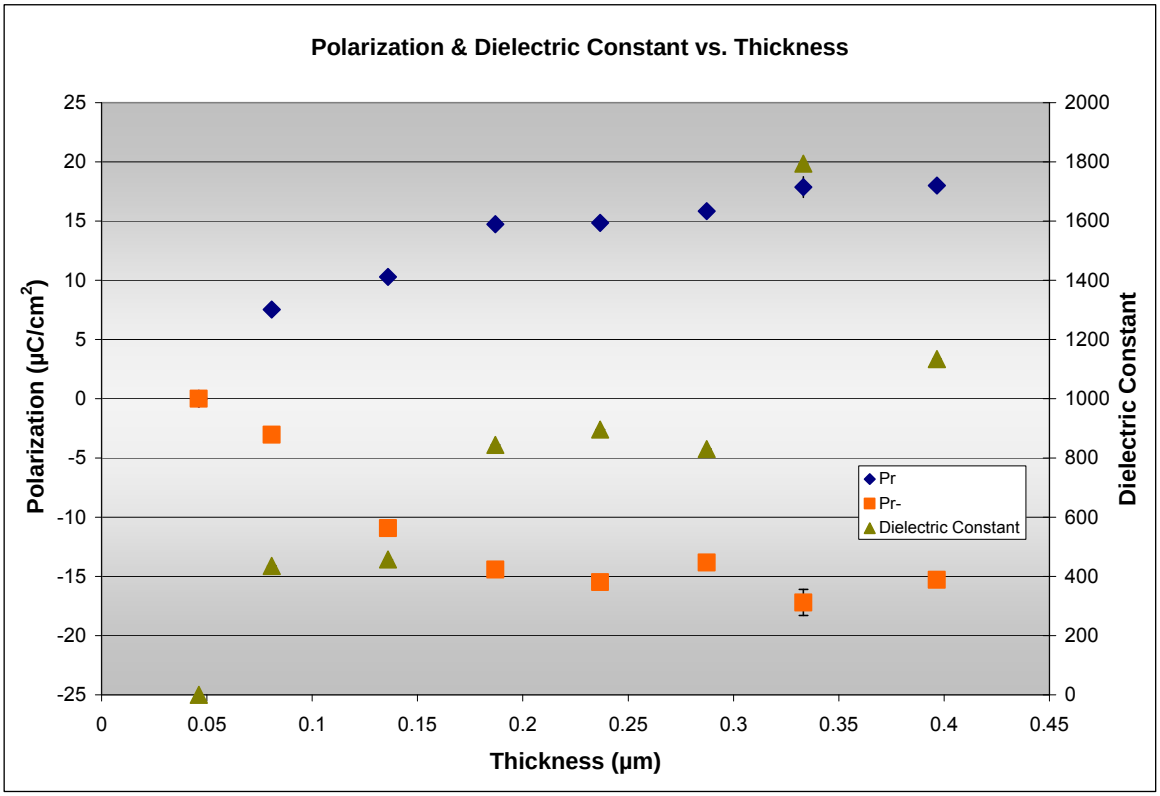

Figure 4. Ferroelectric and dielectric test results for wafer 2151.

NOTE: 1-σ error bars included, but obscured by data point icons.

Wafer 2174, where the Ti and bottom Pt layers were thinned compared to wafer 2151, exhibited a similar trend of decreasing polarizations and dielectric constants with decreasing thickness except for the 3 spin sample (3F), see figure 5. At 1382 Å, this capacitor provided acceptable polarizations although its dielectric constant values were slightly lower than the desired value of 800.

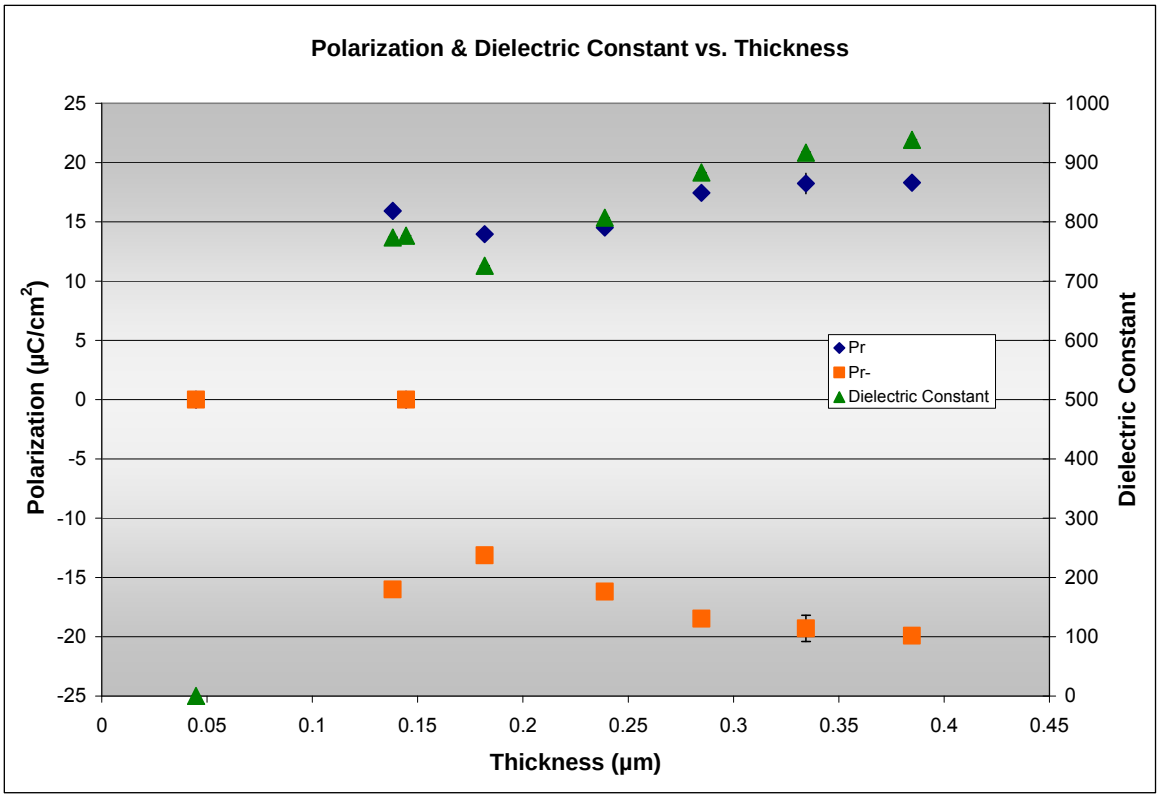

Figure 5. Ferroelectric and dielectric test results for wafer 2174.

NOTE: 1-σ error bars included, but obscured by data point icons.

Wafer 2156 also yielded similar performance trends as the other two wafers, but also had anomalously well-performing capacitors at 4 spins, at a thickness of 1869 Å, see figure 6. This capacitor had polarizations well over 20 μC/cm^2, along with a dielectric constant in the range of 800. Further testing is ongoing to assess the validity of the 4 spin data.

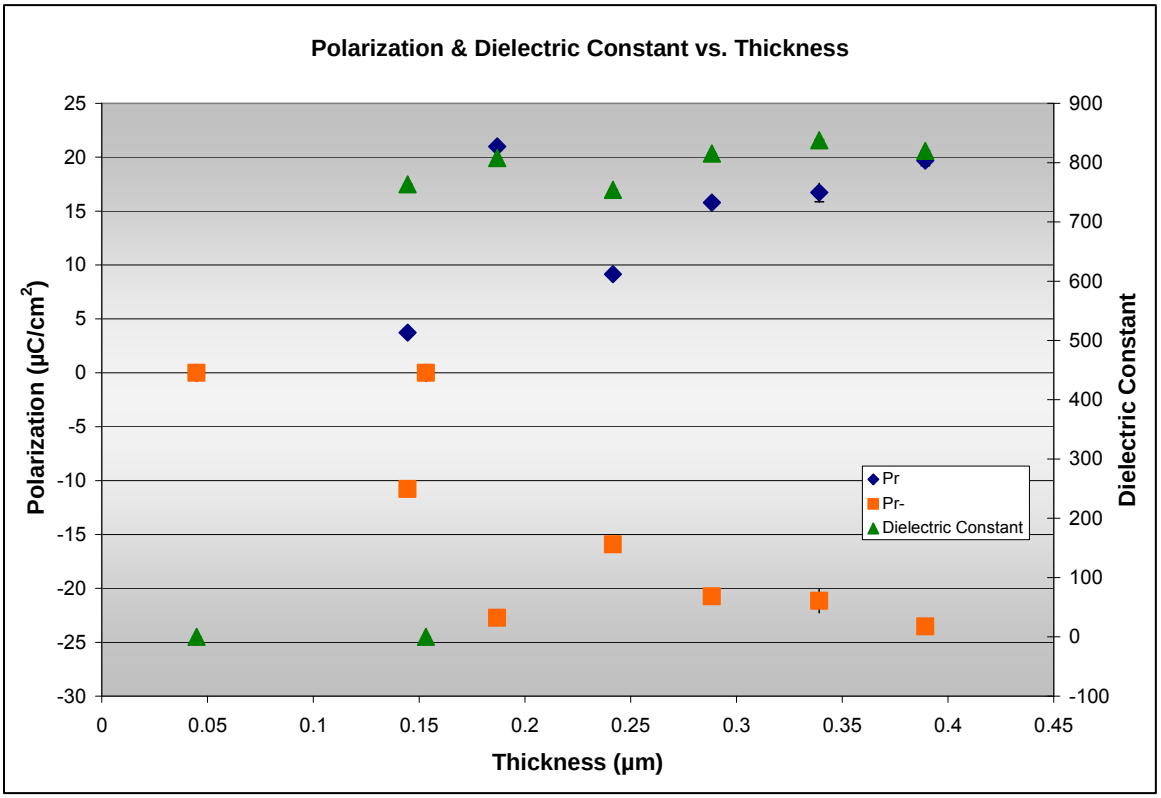

Figure 6. Ferroelectric and dielectric test results for wafer 2156.

NOTE: 1-σ error bars included, but obscured by data point icons.

Selected hysteresis loops for wafer 2156 can also be figure 7. Notice the breakdown of the hysteresis loop from its ideal shape as well as a loss of remanent polarizations from 5E (1869 Å) to 5G (1532 Å), the point at which ferroelectric performance sharply declined.

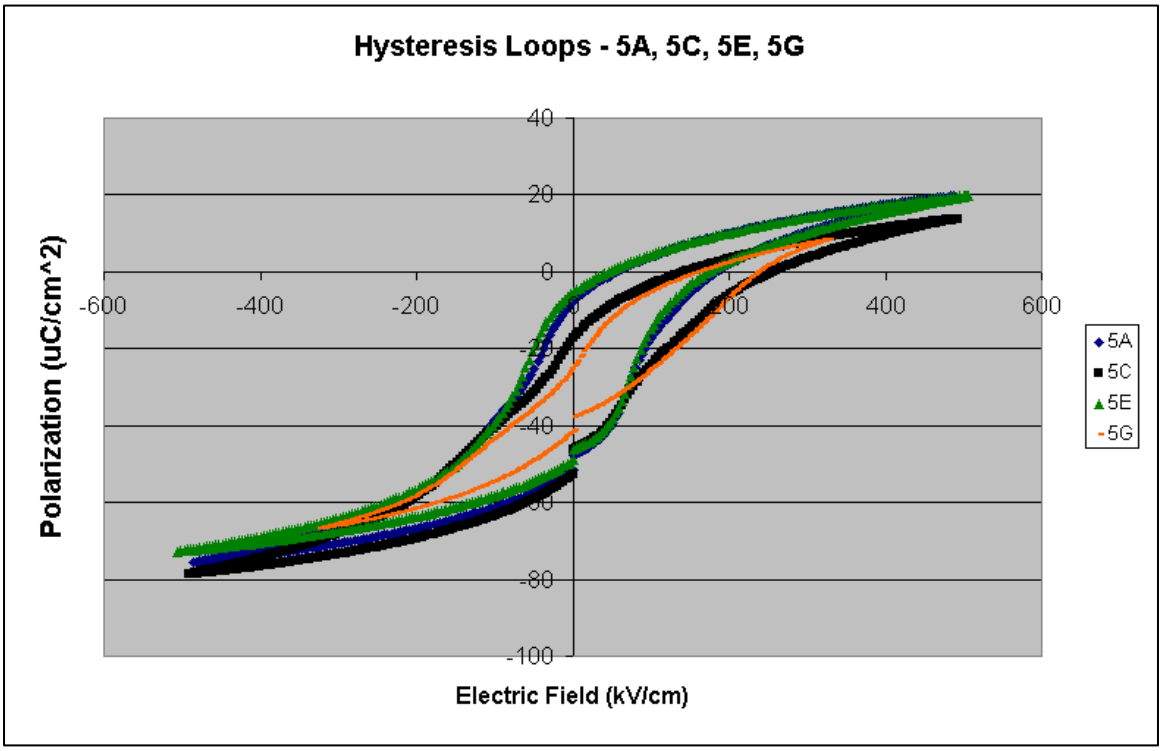

Figure 7. Selected hysteresis loops for wafer 2156.

3.2 Spin Rate Test

The first part of the spin rate test investigated the thickness of deposited PZT as a function of spin rate. The second part, investigating the dielectric and ferroelectric properties as a function of spin rate, was not completed, and will be left for future work. The results of the first part can be found in figures 9 and 10. Sol-gel solution 191 was to be tested, but yielded poor test samples because of excessive crystal formation, likely due to drying of the solution. New test samples will be prepared for spin rate testing of this solution during future experiments. Figure 8 shows the effects of differing solution molarity. Per spin, solution 192 deposits more PZT than solution 190, owing to its higher molarity. Figures 9 and 10 show all the thicknesses up to 4000 Å by spin for solution 190 and 192, respectively. The preliminary results of the spin rate test show that increasing the spin rate from 3000 to 5000 rpm is indeed a viable method of reducing device thickness. Whether acceptable performance is maintained depends on the dielectric and ferroelectric tests of the spin rate samples.

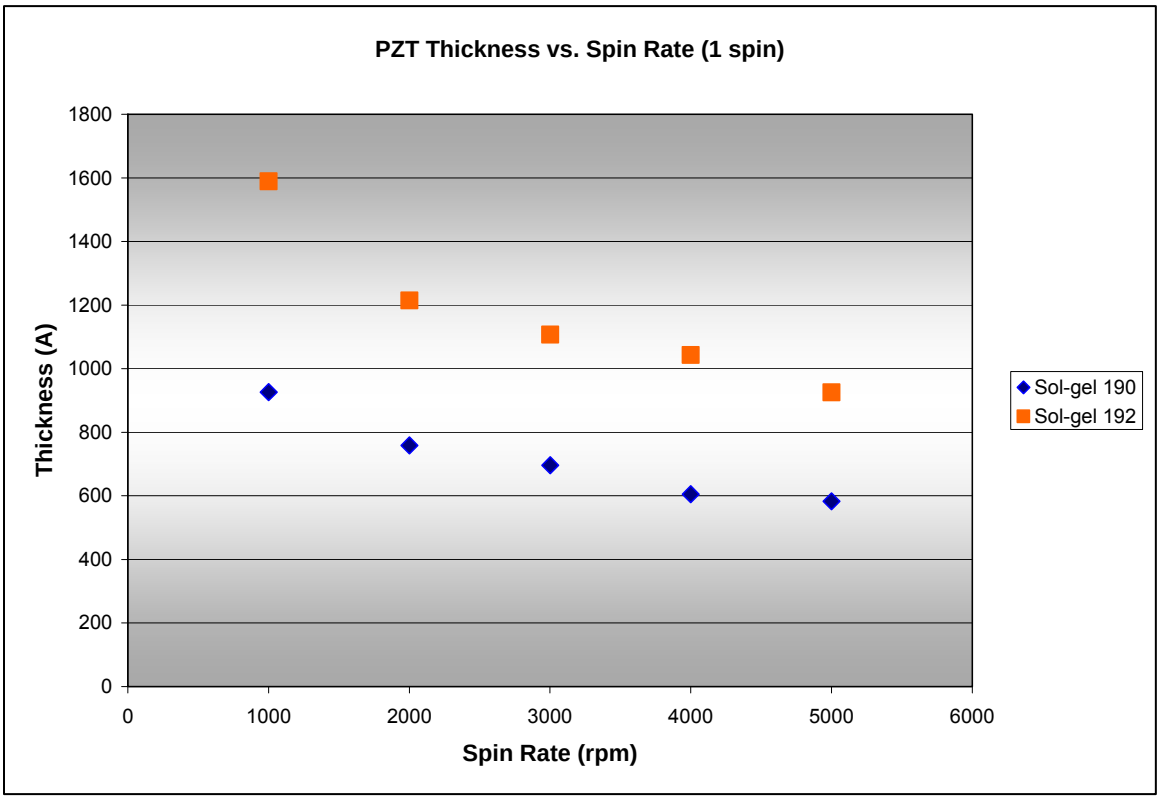

Figure 8. Thicknesses after 1 spin for various spin rates and PZT sol-gel solutions.

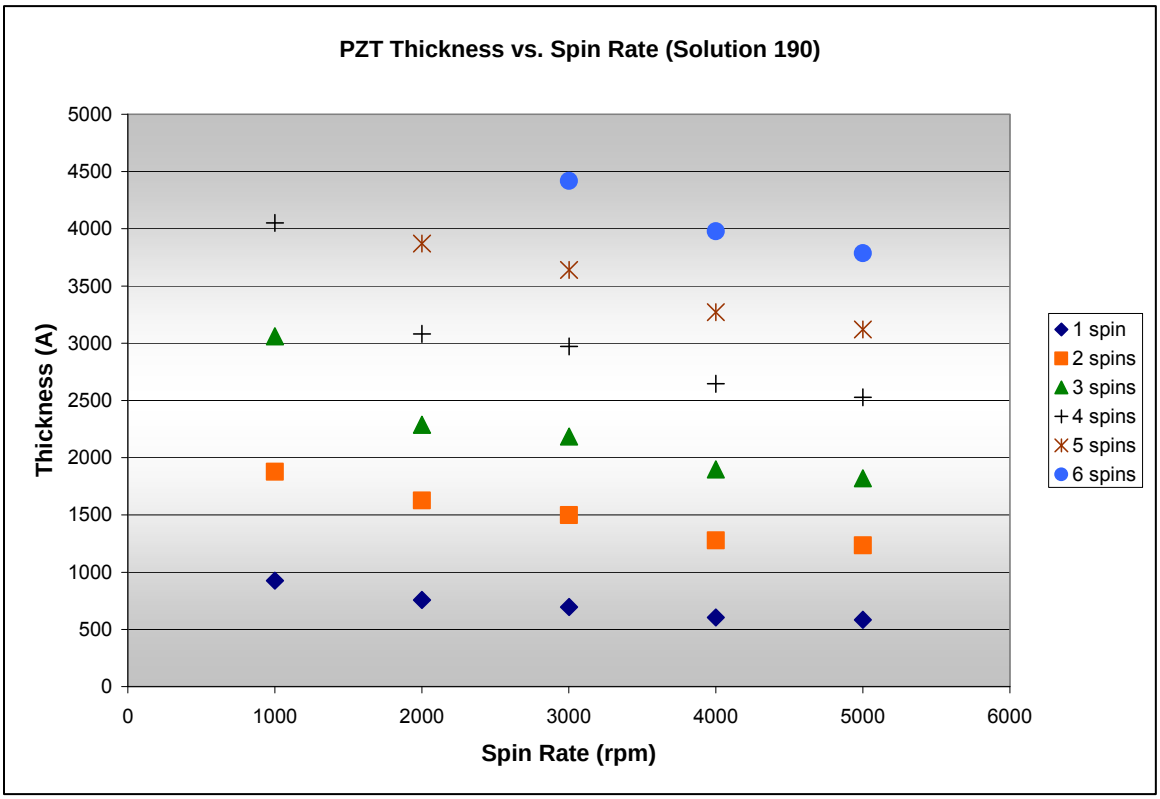

Figure 9. Thicknesses by spin for sol-gel solution 190.

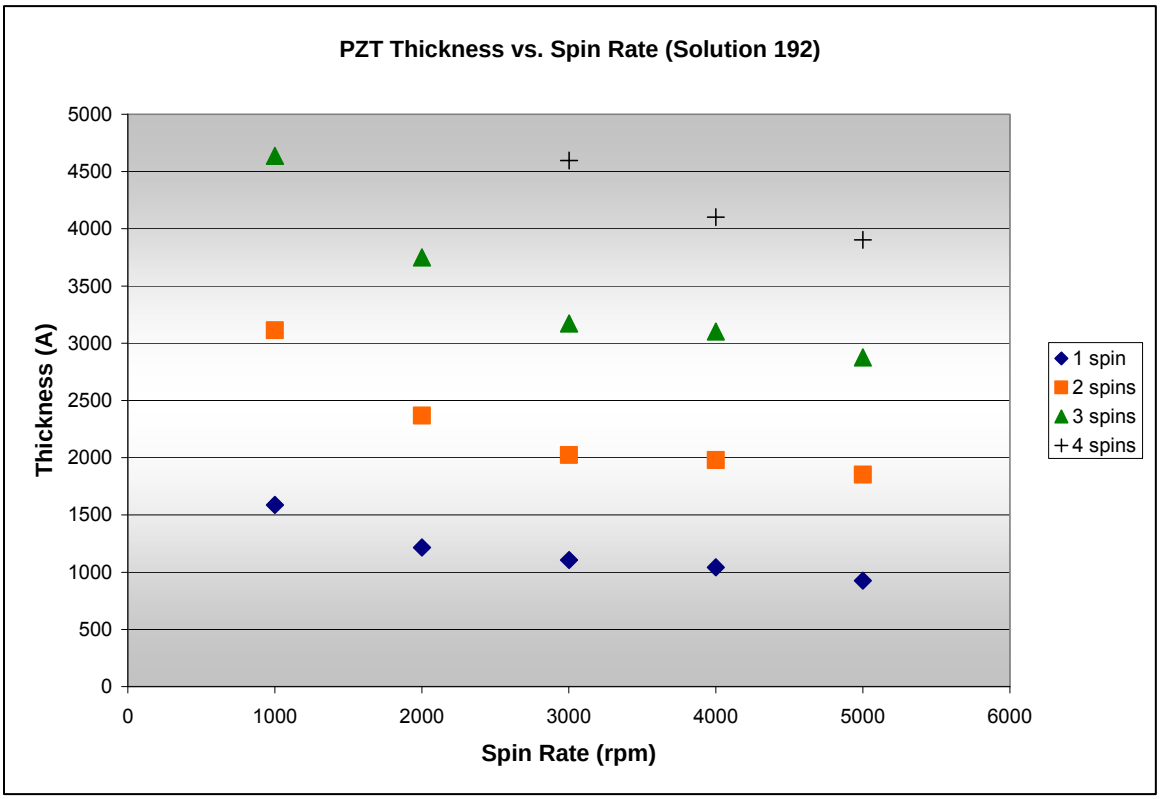

Figure 10. Thicknesses by spin for sol-gel solution 192.

3.5 Sol-gel PZT Solution Test

Table 5. Sol-gel PZT solution test results.

Sol-gel	Pr (μC/cm^2)	Pr- (μC/cm^2)	Capacitance (nF)	D	ε_{33}
190	19.93	-19.83	4.735	0.0306	1122
191	15.66	-15.28	5.315	0.0183	954
191 (2221)	18.52	-16.91	10.389	0.0316	893
192	15.44	-15.21	3.568	0.0309	1306

The results of solution testing with PZT sol-gels of varying molarity can be found in table 5. The data suggests that solution 190, with a molarity of 0.367, has the best overall performance because of a high dielectric constant and remanent polarizations. This agrees with past results from ARL's sol-gel PZT processing.

4. Summary and Conclusion

The results of this project show that film thickness can be minimized to between 1800 Å and 2200 Å while maintaining an acceptable level of ferroelectric performance for the NEMS program. Below 1800 Å, a noticeable general degradation in performance is observed. Reduction of bottom electrode thickness and PZT thickness (by number of spins or spin rate) are, for the most part, viable methods of reducing device thickness. The molarity test data, which showed that sol-gel 190 produced the best ferroelectric performance, coupled with imminent with a molarity of 0.367, will provide a basis for further work in improving performance below 1800 Å.

Symbols, Abbreviations, and Acronyms

Å	Angstrom
ARL	U.S. Army Research Laboratory
cm	centimeter
CMOS	complementary metal-oxide semiconductor
DARPA	Defense Advanced Research Projects Agency
DC	direct current
kHz	kilohertz
Krpm	kilo rotations per minute
min	minute
mm	millimeter
NEMS	nanoelectromechanical system
Pt	platinum
PZT	lead zirconate titanate
rpm	revolutions per minute
RTA	rapid thermal anneal
s	second
sccm	standard cubic centimeters per minute
SiO_2	silicon oxygen
Ti	titanium
UV	ultraviolet
μm	micrometer
Zr	zirconium

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